



Combined effect of KCl and SO₂ on the selective catalytic reduction of NO by NH₃ over V₂O₅/TiO₂ catalyst



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ABSTRACT

In recent years, the alkali metal-induced deactivation of V₂O₅/TiO₂ catalysts during the selective catalytic reduction (SCR) of NO by NH₃ has received much attention. The presence of SO₂ in flue gas may influence the alkali metal-induced deactivation because of its possible interactions with catalysts and alkali metals. This study aims to evaluate the combined effect of SO₂ and alkali metals on the SCR activity of V₂O₅/TiO₂ catalysts and identify the compound responsible for catalyst deactivation. KCl, the typical alkali substance in flue gases, was doped to in-house prepared V₂O₅/TiO₂ catalysts by impregnation, and the KCl to V₂O₅/TiO₂ (K/V) molar ratio was controlled at 0–0.3. The catalysts were subjected to the activity test for >120 h and characterized by BET, XPS, and FTIR. The results indicate that SO₂ increases the deactivation of V₂O₅/TiO₂ catalysts by KCl, and the increased extent depends on the amount of KCl deposited on the catalyst. At a K/V molar ratio of 0.1, K₂S₂O₇ was formed and interacted with V₂O₅ to produce a eutectic; however, at a K/V ratio of 0.3, the eutectic was not observed. This eutectic significantly decreased NH₃ adsorption, particularly those on Brønsted acid sites, and weakened the oxidation ability of the catalyst, thus significantly decreasing the SCR activity.

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1. Introduction

The selective catalytic reduction (SCR) of NO_x by NH₃ is an efficient method for the reduction of NO_x in stationary flue gas. V₂O₅/TiO₂ catalyst containing 1.0–2.0 wt% V₂O₅ and 5–8 wt% WO₃ has been widely used for SCR because of its high activity/selectivity and resistance to SO₂ poisoning at 350–450 °C. To meet the temperature requirement of catalyst, SCR equipment is installed at the upstream of the dust precipitators, causing unavoidable deactivation of the catalyst by fly ash due to plugging, masking of the active components, attrition, and erosion [1,2]. To explain the deactivation results of full-scale plants, various compounds present in the fly ash were doped separately to the catalyst by wet impregnation or deposited separately on the catalyst by injecting their aerosols [3–10]. Most of these studies indicated that alkali metals, particularly potassium, were mainly responsible for the deactivation of SCR catalyst [4,7–10].

The deactivation of V₂O₅/TiO₂ catalyst by alkali metals has been extensively investigated by lab or pilot-scale experiments [2–4,7–9]. Kling et al. [9] studied high-dust SCR catalysts in a pilot boiler and found that the deposition of ultrafine alkali particles

(<100 nm) is mainly responsible for deactivation of the catalyst. Zheng et al. [10] reported that both the chemical poisoning of active sites and the physical blocking of the outer wall surface deactivated the catalyst, but the former was the main reason. Chen and Yang [11] mentioned the interactions of potassium with V₂O₅ active phase and reported that the amount of ammonia adsorbed on the Brønsted acid sites of V–OH decreased with increasing amount of potassium deposited on the catalyst, which was later supported by several studies [3,4,8,10,12–15]. Moreover, Lisi et al. [12] reported that catalyst deactivation was proportional to the number of acid sites neutralized by alkali metals, and Chen et al. [8] reported that the poisoning effect of alkali metals correlated to the reducibility of vanadium and tungsten species besides surface acidity.

Although several studies supported the viewpoint that the interaction of alkali metals with V₂O₅, decreasing the Brønsted acidity, was responsible for the deactivation of SCR catalyst, it is still unclear in what form alkali penetrates and reacts with V₂O₅/TiO₂ catalyst. Importantly, most of the studies except the pilot-scale studies have been conducted in the absence of SO₂, and some characterizations have been performed on a fresh catalyst added with catalyst-poisoning compounds. However, the flue gas in fossil-fuel-fired power plants usually contains a certain amount of SO₂, and the interaction of SO₂ with alkali metals may change their separate effects on the SCR activity, particularly after a long running time. Because the combined effect of SO₂ and alkali metals on SCR

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has been rarely studied, this study aims to investigate this effect using KCl as the poisoning compound and elucidate the deactivation mechanism by the detailed analysis of fresh and used catalysts.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared in-house by extruding a paste containing TiO_2 - WO_3 powder, two binders, and an aqueous solution of NH_4VO_3 in oxalic acid into cylinders, followed by drying at 110°C for 12 h and calcining at 450°C for 5 h. The two binders were polyvinyl alcohol (PVA) and bentonite clay. The TiO_2 - WO_3 powder was prepared by mixing TiO_2 powder (Veking, Hangzhou, China) with an aqueous solution of ammonium paratungstate, $(\text{NH}_4)_{10}(\text{H}_2\text{W}_{12}\text{O}_{42})\cdot 4\text{H}_2\text{O}$, drying the slurry at 110°C for 4 h and calcining at 320°C for 2 h. The composition of the catalyst was mainly controlled by the concentration and amount of NH_4VO_3 and ammonium paratungstate, which is expected to be 1 wt% V_2O_5 , 5 wt% WO_3 , 74 wt% TiO_2 , and 20 wt% bentonite.

The cylindrical catalyst was ground and sieved to 20–40 mesh, and KCl was doped to the catalyst particles by pore-volume impregnation, followed by drying at 110°C . The potassium loading was adjusted by changing the KCl concentration.

2.2. Activity test

The activity of the catalysts was investigated using a fixed-bed quartz reactor. $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst (20–40 mesh, 3 mL) in the reactor was heated to 400°C under a N_2 stream. At the steady state, the N_2 stream was replaced by 500 ppm NO, 500 ppm NH_3 , 1500 ppm SO_2 , 5.0 vol% O_2 , 5.0 vol% H_2O , and the balance by N_2 . The total gas flow rate was maintained at 400 mL/min, corresponding to a gas hourly space velocity (GHSV) of 8000 h^{-1} . The concentrations of SO_2 , NO, and O_2 in the feed and effluent were monitored online using a flue gas analyzer (KM9106 Quintox, Kane) or a mass spectrometer (MS, Omnistar 200, Switzerland).

2.3. Catalyst characterization

The composition of the catalyst without KCl was determined by X-ray fluorescence (XRF) spectrometry (S4-Explorer, Bruker, Germany). The K and V contents in all the catalysts were determined by inductively coupled plasma (ICP) optical emission spectroscopy (ICAP 6300, Thermal Scientific, USA).

The specific surface area and pore volume of the catalysts were determined by N_2 adsorption at 77 K using a Quadrasorb SI-MP analyzer (Quantachrome, USA). Prior to the analysis, the samples were degassed under vacuum at 300°C for 11 h. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) method with P/P_0 between 10^{-8} and 1. The pore distribution was obtained from the desorption data by Barrett–Joyner–Halenda (BJH) method.

The chemical forms of the main elements in the catalysts were determined by X-ray photoelectron spectroscopy (XPS) measurements using an ESCALAB 250 spectrometer (Thermo Fisher Scientific Company, USA) at room temperature with monochromated Al $\text{K}\alpha$ radiation ($h\nu = 1486.6\text{ eV}$) at $15\text{ kV} \times 200\text{ W}$. The binding energies were corrected by the C1s peak at 284.8 eV. XPS data analysis was performed using an XPS-Peak program, and the spectra were fitted with the optimal Gaussian/Lorentzian ratio after the subtraction of a Shirley-type baseline.

The NH_3 adsorption capacities of the catalysts were measured using an *in situ* diffuse-reflectance infrared Fourier transform spectrometer (DRIFTS, Nicolet 6700, Thermo Fisher Scientific, USA) coupled with a mass spectrometer (MS, Omnistar 200, Switzerland). The catalysts were ground and loaded to the ceramic

Table 1

Composition of the fresh catalyst without KCl deposition.

Component	TiO_2	WO_3	V_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O
Amount (wt%)	73.8	5.3	0.89	10.3	3.5	2.3	0.93	0.50	0.18

frit in the *in situ* reaction cell coupled with ZnSe optical windows without packing or dilution and then heated to 400°C at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 flow (100 mL/min). At the steady state, a single-beam spectrum was recorded by accumulating 64 scans at a resolution of 4 cm^{-1} using an MCT detector and a KBr beam splitter. Then, the N_2 flow was replaced by 0.1% NH_3/N_2 flow for NH_3 adsorption, and FTIR spectra were recorded irregularly in the Kubelka–Munk (K–M) mode with the single-beam spectrum as the background until the NH_3 signal detected by MS did not change.

The temperature-programmed desorption (TPD) and oxidation (TPO) of NH_3 were also performed by DRIFTS-MS. The catalysts loaded in the ceramic frit were heated to 110°C under a flow of Ar and held for 30 min to remove moisture (pretreatment). Then, the sample was subjected to an NH_3/Ar flow (0.1% NH_3) for *in situ* NH_3 adsorption for 20 min and purged with Ar until no NH_3 was detected in the effluent. Finally, TPD was performed under Ar flow (100 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$ until 450°C . For the TPO experiment, the catalyst samples were pretreated as mentioned above and then heated to 450°C at $10^\circ\text{C}/\text{min}$ under a flow containing 5% O_2 and 0.1% NH_3/Ar . In the entire process, the effluent was analyzed by MS.

3. Results and discussion

3.1. Catalyst composition and code

The composition of the fresh catalyst determined by XRF is shown in Table 1. The TiO_2 , V_2O_5 , and WO_3 contents are 73.8%, 0.9%, and 5.3%, respectively, which are close to the set values during the catalyst preparation. In addition to the three main components, the fresh catalyst also contains a certain amount of other inorganic oxides, such as SiO_2 , Al_2O_3 , Fe_2O_3 , and K_2O , because of the bentonite clay binder. Notably, the K/V molar ratio in the fresh catalyst reached 0.2.

The V_2O_5 and K_2O contents in the fresh catalyst determined by ICP were the same as the XRF results. The ICP analysis of the catalysts doped with KCl indicates that the K/V molar ratios excluding the original K_2O are 0.02, 0.1, and 0.3. The K/V ratio of 0.3 was reported to be of the same order of magnitude of alkali metal deposited on SCR catalysts in a thermal power plant after running for 3 years [16] and high enough for a significant chemical deactivation [2].

The catalysts are denoted according to the molar ratio of $\text{KCl}/\text{V}_2\text{O}_5$ such as K/V(0.1) because K_2O was found to have slight influence on the SCR activity (see below). The catalysts that underwent the activity test in presence of SO_2 were denoted as K/V(x)-used.

3.2. Combined effect of SO_2 and KCl on SCR activity

Fig. 1 shows the NO conversions of the different catalysts in the presence and absence of SO_2 . It should be pointed out that for all the runs, neither NO_2 nor N_2O was detected and the N_2 selectivity was about 100%. Fig. 1(A) indicates that in the absence of SO_2 , K-free, K/V(0.02), and K/V(0.3) catalysts exhibit a similar NO conversion (termed X_{NO}) of $\sim 96\%$, while K/V(0.1) catalyst has a lower X_{NO} , $<80\%$. Clearly, the poisoning effect of KCl on the SCR activity occurred only on K/V(0.1) catalyst, but not on K/V(0.02) and

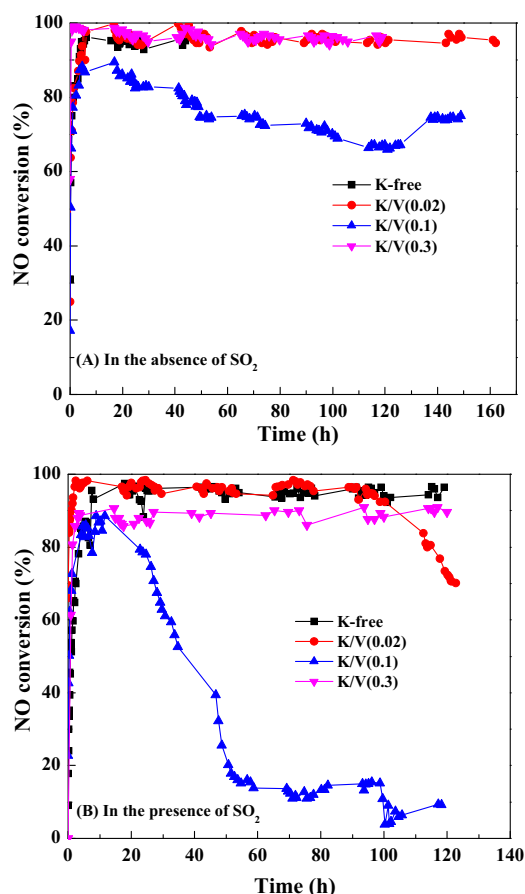


Fig. 1. Effect of KCl and SO₂ on the SCR activity of V₂O₅/TiO₂ catalysts. Conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, 5% H₂O, 1500 ppm SO₂ (when used), GHSV of 8000 h⁻¹, temperature of 400 °C.

K/V(0.3) catalysts in the absence of SO₂. This irregular phenomenon is surprising because most studies indicated a gradual increase in the catalyst deactivation with increasing K/V ratio [3,8,17]. Detailed comparison suggests that this contradiction may be due to the different alkali compound used: KOH with K/V ratio of 0.2–4.0 in the work of Chen et al. [8], K₂CO₃, KHSO₄ and K₂SO₄ with K/V ratio of 0.05–0.2 in the work of Kröcher et al. [3], and KCl with K/V ratio of 0.02–0.3 in our work.

Notably, the X_{NO} of K/V(0.1) is almost the same as those of the other three catalysts in the first 3 h and deviates from them afterwards, indicating that the poisoning effect of KCl depends on the running time. This should be concerned because the activity tests in many lab studies lasted for <1 h [8,18,19], and the deactivation was almost not observed at a K/V ratio of ~0.2 in the time scale [8,17].

A comparison of Fig. 1(A) and (B) indicates that SO₂ did not change the steady-state X_{NO} of K-free catalyst even though this catalyst contained 0.18 wt% K₂O, but decreased the X_{NO} of the catalysts doped with KCl. This indicates that K₂O is not as poisonous as KCl in the presence of SO₂ in this study, probably because K₂O was embedded in the matrix. For K/V(0.02) catalyst, the X_{NO} was maintained at 95% in 100 h in the presence of SO₂ and decreased rapidly afterwards. For K/V(0.1) catalyst, X_{NO} increased to the maximum value within 20 h and then decreased sharply to a steady value of ~10% at 60 h. For K/V(0.3) catalyst, SO₂ decreased its X_{NO} from 95% to 90% in the beginning. Clearly, the combination of KCl and SO₂ caused more deactivation than only KCl. The results shown in Fig. 1(B) further indicate that this combined effect is also a long-term phenomenon.

Table 2

Pore properties of the fresh and used catalysts.

Sample	BET surface area (m ² /g)		Total pore volume (cm ³ /g)	
	Fresh	Used*	Fresh	Used*
K-free	94.7	89.5	0.38	0.37
K/V(0.02)	92.1	80.3	0.37	0.34
K/V(0.1)	89.1	76.8	0.36	0.32
K/V(0.3)	87.3	82.7	0.36	0.35

* The samples collected after the activity test in the presence of SO₂.

3.3. Analysis of the combined effect of KCl and SO₂

3.3.1. Pore properties of the catalysts

In general, the pore properties of the catalysts play an important role in SCR activity. Table 2 shows the pore properties of the fresh and used catalysts to understand the combined effect of SO₂ and KCl on X_{NO}. The addition of KCl slightly reduced the BET surface area of the fresh K-free catalyst, from 94.7 to 92.1 m²/g for K/V(0.02), 89.1 m²/g for K/V(0.1), and 87.3 m²/g for K/V(0.3). The activity tests in the presence of SO₂ further reduced the BET surface areas of all the catalysts. However, the reduced value was only 5–12 m²/g, and the minimum surface area was still 76.8 m²/g (see K/V(0.1)-used), which is much higher than some V₂O₅/TiO₂ catalysts with a high SCR activity [2,10]. Therefore, it is unconvincing to attribute the deactivation of K/V catalysts, particularly K/V(0.1), to the changes in the pore properties.

3.3.2. Chemical states of vanadium in the catalysts

To further investigate the reason for the combined effect of SO₂ and KCl on X_{NO}, the chemical states of vanadium were analyzed by fitting the XPS spectra of V 2p_{3/2} of different catalysts with an optimal Gaussian/Lorentzian ratio, and the results are shown in Fig. S1. The binding energies of V³⁺, V⁴⁺, and V⁵⁺ in different literatures are somewhat different due to the different local environment; however, literature review indicated that those at 516.9–517.3, 515.7–516.3, and 515.0–515.6 eV were generally assigned to V 2p_{3/2} in V₂O₅, V⁴⁺ species, and V₂O₃, respectively [20–29]. It is also recognized that for the same element in the same compound, an increase in oxidation state yields an increase in binding energy in 0.8–1.0 eV/valence. Therefore, the peaks centered at ~517.1 ~516.0, and ~515.0 eV in this work were attributed to V₂O₅, V⁴⁺ species, and V₂O₃, respectively. The V⁴⁺ species may be VO₂ for the fresh catalyst or VOSO₄ for the used catalyst.

Table 3 summarizes the atomic ratio of each type of vanadium in different catalysts. It indicates that the vanadium in fresh K-free catalyst exists in three forms: V₂O₅, VO₂, and V₂O₃, indicating the partial reduction of V⁵⁺ to a lower valence species during the preparation. However, the V³⁺ species disappears in the used K-free catalyst, and the vanadium exists only in two forms: V⁴⁺ (VO₂ or VOSO₄) and V₂O₅, indicating the complete oxidation of V₂O₃ during the activity test. The high steady X_{NO} of K-free catalyst (Fig. 1) indicates that the presence of V₂O₃ in the beginning does not affect the SCR activity. The vanadium in fresh K/V(0.02) and K/V(0.1) catalysts also exists in three forms (V₂O₅, VO₂, and V₂O₃), and V₂O₃

Table 3

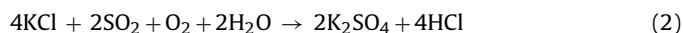
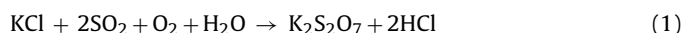
Chemical states of vanadium in the fresh and used catalysts.

Sample	V ⁵⁺ content (%)		V ⁴⁺ content (%)		V ³⁺ content (%)		V2p _{3/2} at 518 eV (%)	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
K-free	30	39	52	61	18	0	0	0
K/V(0.02)	21	15	48	42	32	0	0	26
K/V(0.1)	12	28	60	37	19	0	9	35
K/V(0.3)	48	35	52	65	0	0	0	0

also disappears after the activity test, similar to those observed for K-free catalyst. However, there is an additional peak at 518.0 eV in used K/V(0.02) and K/V(0.1) catalysts compared to the used K-free catalyst, indicating the formation of a new vanadium compound during the activity test in the presence of SO₂. For K/V(0.3) catalyst, only two forms of vanadium, V₂O₅ and VO₂, were detected on the fresh catalyst, and the peak at 518.0 eV was not observed on the used catalyst. Combining the vanadium state and activity of the catalysts shown in Fig. 1(A), we found that when the fresh catalyst contained V₂O₃, the X_{NO} gradually increased in the first 5 h probably because of the oxidation of V₂O₃, see: K-free, K/V(0.02), and K/V(0.1). Importantly, the new vanadium species formed during the activity test in the presence of SO₂ may be responsible for the lower X_{NO} of K/V(0.02) and K/V(0.1) catalysts (Fig. 1(B)). Therefore, the confirmation of the new vanadium species is important to understand the deactivation mechanism of the catalyst.

The binding energy of the V 2p_{3/2} of the new vanadium species (518.0 eV) is higher than that of V₂O₅ (517.0 eV), indicating that the vanadium in the new species is most probably V⁵⁺, and the anion correlating to the vanadium is more electronegative than O²⁻. Moreover, the amount of potassium affects the formation of the new vanadium species because it was observed in K/V(0.02) and K/V(0.1) catalysts, but not in K-free and K/V(0.3) catalysts. Kamata et al. reported that vanadium species may react with K₂O to form KVO₃ at a K₂O loading of 2.0% [17]. Folkmann et al. reported the formation of the eutectics of V₂O₅ and K₂S₂O₇ at temperatures <400 °C [30]. Because the activity test was performed in the presence of SO₂, the latter is more preferable. When this happens, the binding energy of V⁵⁺ should shift to a higher value because of the stronger electronegativity of S₂O₇²⁻ than O²⁻.

To determine whether S₂O₇²⁻ was formed in the different catalysts, the XPS spectra of the S 2p of different used catalysts are shown in Fig. 2. Two S 2p_{3/2} peaks are observed for the used K-free and K/V(0.3) catalysts, located at 168.9 ± 0.1 and 170.1 eV, and can be assigned to SO₄²⁻ in different chemical environments. The former may be K₂SO₄ or VOSO₄ [31], and the latter may be H₂SO₄ [32]. For the used K/V(0.02) and K/V(0.1) catalysts, an additional peak at ~168.3 eV was observed in addition to those at 168.8 ± 0.1 and 170.1 eV, which can be assigned to S₂O₇²⁻ [33]. This indicates that S₂O₇²⁻ is formed in used K/V(0.02) and K/V(0.1) catalysts, but not in used K/V(0.3) catalyst, consistent with the theoretical analysis, i.e., the formation of K₂S₂O₇ or K₂SO₄ depends on the molar ratio of KCl to SO₂. K₂S₂O₇ may be formed through Reaction (1) at a lower KCl/SO₂ ratio, while K₂SO₄ may be formed through Reaction (2) at a higher KCl/SO₂ ratio. However, the XPS of K 2p was very noisy because of a low potassium loading and could not provide convincing evidence. To confirm different sulfur species in different used catalysts, temperature-programmed heating was performed, and the SO₂ release profile was recorded. The results shown in Fig. 3 indicate that the SO₂ release of the used K/V(0.1) catalyst is very large and starts at a lower temperature, followed by the used K/V(0.02) catalyst. These phenomena may provide an indirect evidence for the formation of the eutectic in these two catalysts.



To further verify the influence of K₂S₂O₇ on V₂O₅ binding energy, V₂O₅ powder was mixed with K₂S₂O₇ or K₂SO₄ and then treated in muffle at 400 °C for 1 h. The obtained samples were characterized by XPS measurement. The results in Fig. 4 indicate that the binding energy of V 2p_{3/2} in V₂O₅ shows little shift when V₂O₅ is calcined with K₂SO₄, but it shows an obvious shift when V₂O₅ is calcined with K₂S₂O₇, from ~516.6 eV for V₂O₅ to ~517.4 eV for V₂O₅-K₂S₂O₇ sample. Although the V 2p_{3/2} peak in V₂O₅-K₂S₂O₇ sample is lower than that of the K/V(0.1)-used, 518.0 eV,

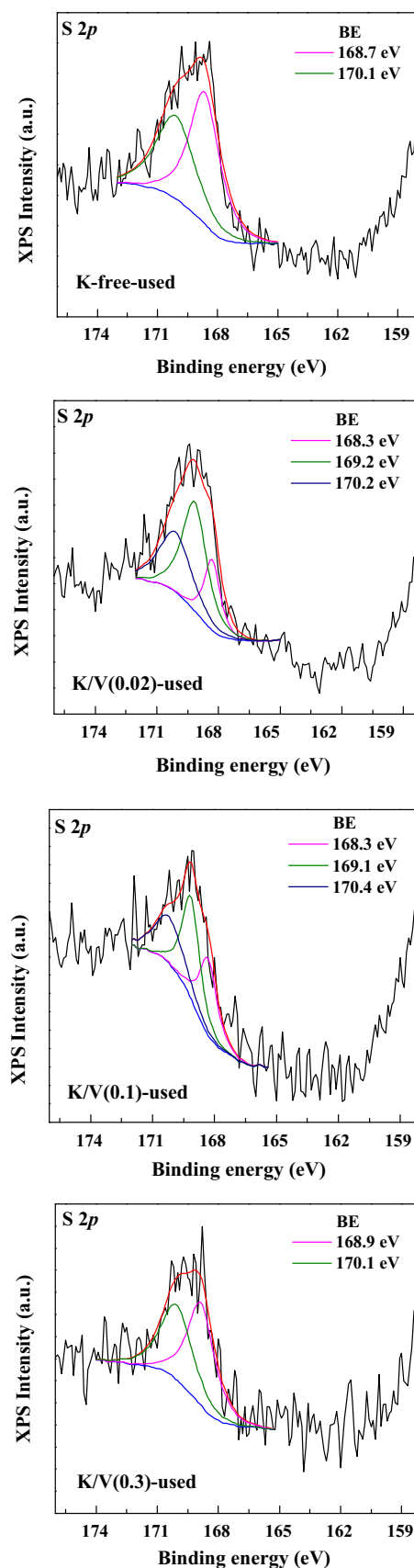


Fig. 2. XPS spectra of S 2p of the different used catalysts.

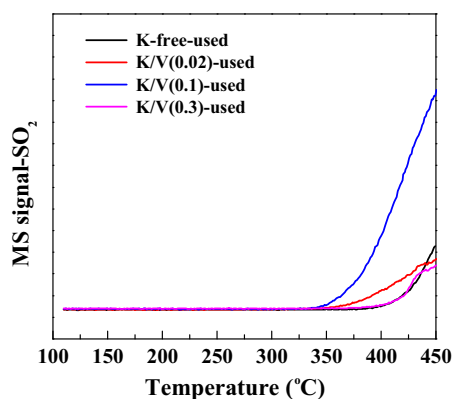


Fig. 3. SO_2 release profiles during temperature programmed heating of the different used catalysts in Ar.

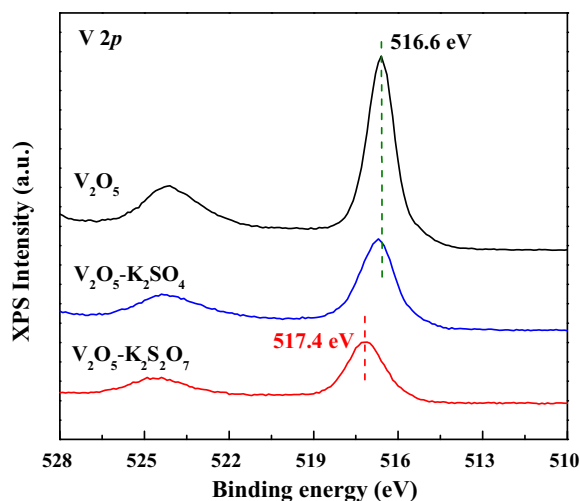


Fig. 4. Effect of $\text{K}_2\text{S}_2\text{O}_7$ and K_2SO_4 on V 2p of V_2O_5 .

possibly due to the different ratio or treatment time, the observation herein is sufficient to evidence that the electron density of V_2O_5 is influenced by $\text{K}_2\text{S}_2\text{O}_7$ but not by K_2SO_4 .

3.3.3. Chemical state of titanium in the catalysts

To evaluate the stability of the TiO_2 support, the XPS spectra of the Ti 2p of different fresh and used catalysts are shown in Fig. 5. All the catalysts exhibited two binding energy peaks at 458.4 and 464.2 eV, which were assigned to the $2p_{3/2}$ and $2p_{1/2}$ of Ti^{4+} species, respectively [20,34]. The same location of the Ti 2p peaks for all the catalysts indicates that KCl may have no interaction with the support, which is different from the DFT result of Lewandowska et al. [35]. Moreover, the Ti $2p_{3/2}$ peaks of all the fresh catalysts are slightly lower than that of the pure TiO_2 , 459.0 eV [36], indicating a higher electron density around Ti or that the electronegativity of the anion correlated to Ti is weaker than that of O^{2-} . This may be caused by the interaction of TiO_2 with V or W species, similar to the results of $\text{V}_2\text{O}_5/\text{ZrO}_2$ catalysts reported by Adamski et al. [37] and Balikdjian et al. [21].

The binding energies of the Ti $2p_{3/2}$ of all the catalysts shifted to higher values after the activity tests in the presence of SO_2 . The degree of shift for K-free, K/V(0.02), K/V(0.1), and K/V(0.3) were 0.3, 0.5, 0.5, and 0.2 eV, respectively. These shifts indicate a decrease in the electron density around Ti during the activity tests. This is probably because of the entry of oxygen into the lattices of the catalysts as evidenced by the oxidation of V^{3+} . Anyway, TiO_2 was stable, and the potassium salt had no effect on its state before and after the

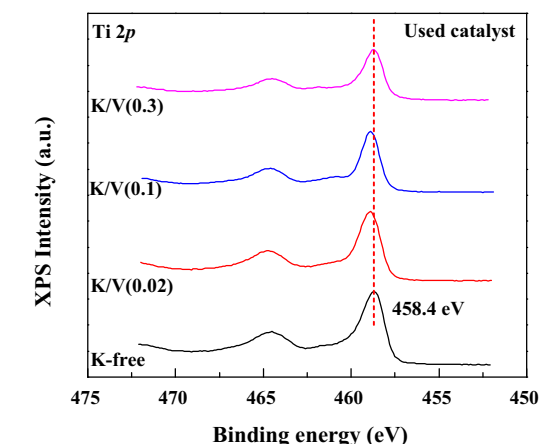
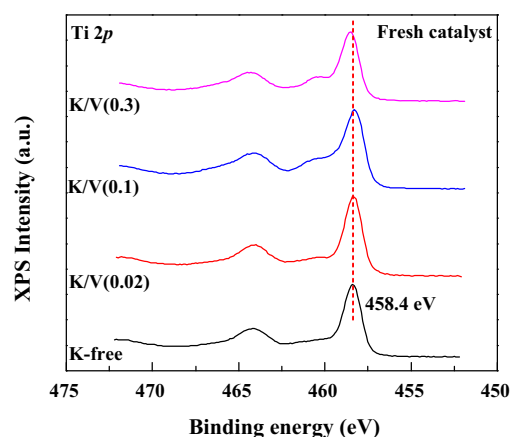


Fig. 5. XPS spectra of Ti 2p for the different fresh and used catalysts.

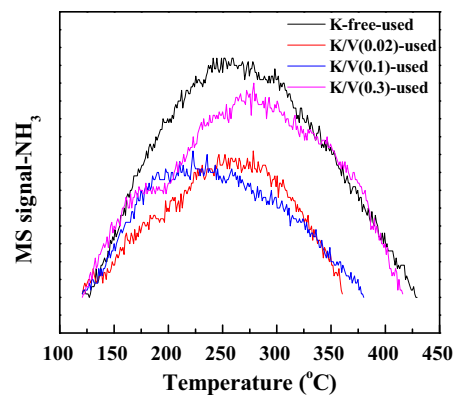
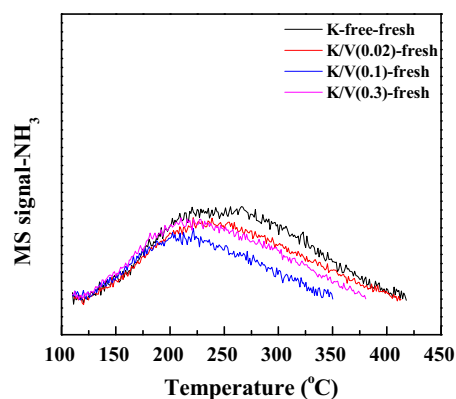


Fig. 6. NH_3 release curves of the different fresh and used catalysts during TPD after saturating with NH_3 .

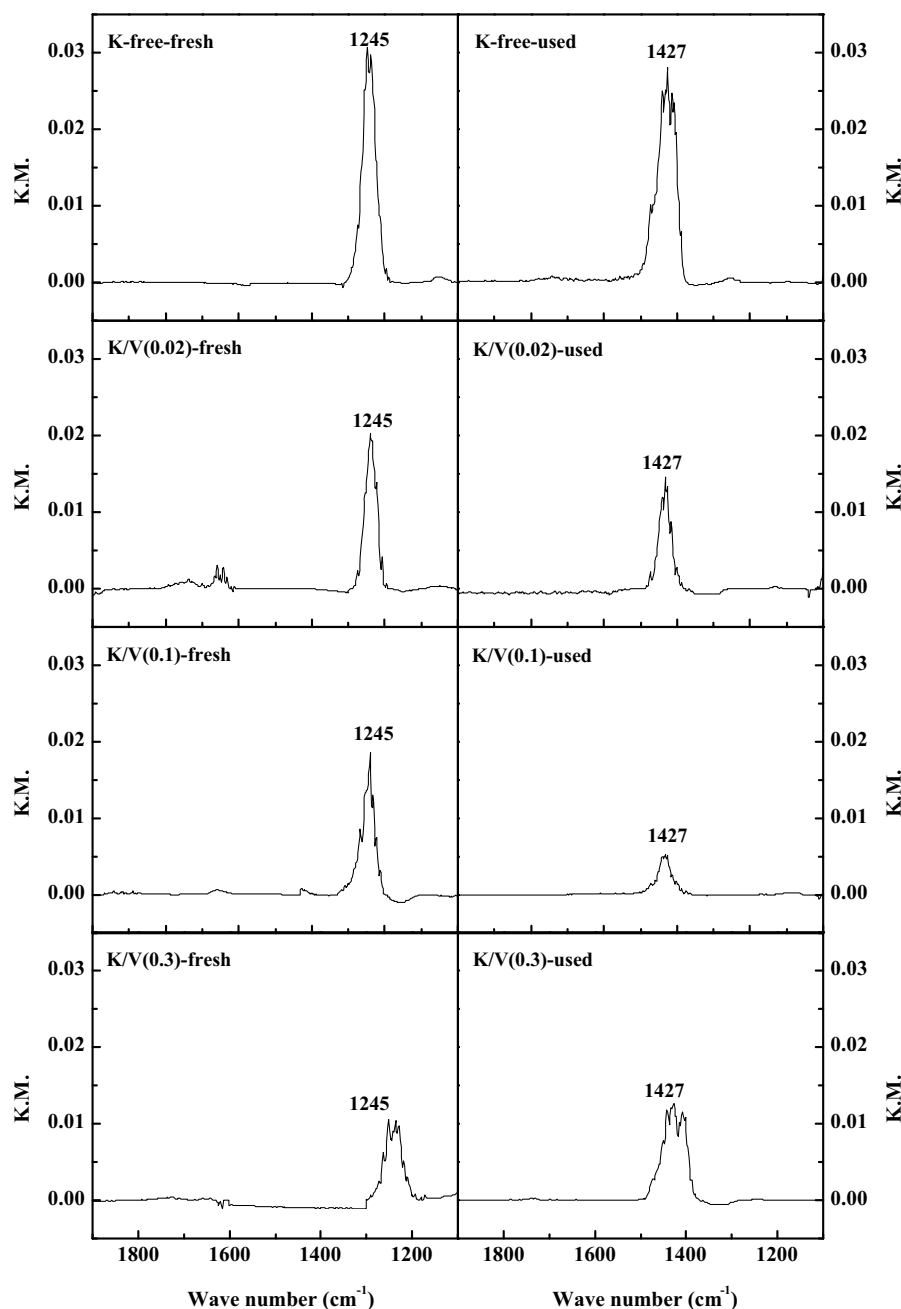


Fig. 7. DRIFT spectra collected during NH_3 adsorption on the fresh and used catalysts at 400°C .

activity tests, indicating that the deactivation of the catalysts by KCl and SO_2 is irrelevant to the TiO_2 support.

The data presented so far indicate that the deactivation of the SCR catalyst by KCl in the presence of SO_2 was because of the formation of $\text{V}_2\text{O}_5\text{-K}_2\text{S}_2\text{O}_7$ eutectic. It is reasonable that the eutectic formation along with V_2O_5 oxidation will decrease the BET surface area of the catalysts. Their concurrence in K/V(0.02) and K/V(0.1) catalysts caused more loss of BET surface area compared to K-free and K/V(0.3) catalysts, explaining the results shown in Table 2.

3.3.4. NH_3 adsorption and oxidation

Although the formation of $\text{V}_2\text{O}_5\text{-S}_2\text{O}_7^{2-}$ eutectic decreased the BET surface area, it could not explain the severe deactivation of K/V(0.02) and K/V(0.1) catalysts in the presence of SO_2 , as analyzed in Section 3.3.1. To investigate the fundamental reason, the NH_3

adsorption capacity and oxidation behaviors of different catalysts were compared.

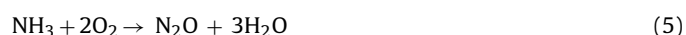
The NH_3 adsorption capacity of a catalyst was measured by TPD after saturating with NH_3 . During the TPD process, no other nitrogen-containing compound except NH_3 was observed. Fig. 6 shows the NH_3 release curves of different fresh and used catalysts. Clearly, the amount of NH_3 released from all the used catalysts are more than those of fresh counterparts, indicating that the surface acidities of all catalysts were enhanced after activity test in the presence of SO_2 . However, these data are not enough to judge what results in the enhanced surface acidity because both sulfation of the catalyst and transformation of V^{3+} to V^{5+} possibly happened. Therefore, NH_3 -TPD of K/V(0.02) and K/V(0.1) catalysts undergoing the activity test in the absence of SO_2 was performed and the results are shown in Fig. S2. It is clear that NH_3 release follows the order: the used catalyst in the presence

of SO_2 » the used one in the absence of SO_2 » the fresh, suggesting that SO_2 in the feed during activity test significantly strength surface acidity of the catalyst, as reported by some researchers [38,39].

To identify the types of acid sites on catalyst surface, NH_3 adsorption at 400°C was performed using a DRIFT spectrometer and the results are shown in Fig. 7. It can be seen that all the fresh catalysts exhibit only one band at 1245 cm^{-1} , assigned to the symmetric bending vibration of NH_3 coordinated on Lewis acid site [40,41], while all the used catalysts in the presence of SO_2 exhibited only one band at 1427 cm^{-1} , assigned to the asymmetric bending vibration of NH_4^+ adsorbed on Brønsted acid sites [42]. Surprisingly, the catalysts that underwent the activity test in the absence of SO_2 present two FTIR peaks at 1427 and 1612 cm^{-1} , respectively (Fig. S3). The peak at 1612 cm^{-1} can be assigned to the asymmetric bending vibration of NH_3 coordinated on Lewis acid site [43,44]. These observations indicate complex transformation of the acid sites: some from Lewis to Brønsted when the activity test was in the absence of SO_2 possibly due to H_2O in the feed [45,46], and almost all from Lewis to Brønsted when the activity test was in the presence of SO_2 due to sulfation of the catalyst.

Comparison of the FTIR peak intensities of fresh and used catalysts shown in Fig. 7 indicates that the activity test in the presence of SO_2 has little effect on or decrease the amount of NH_3 adsorbed at 400°C , although an obvious enhancement of surface acidity was observed by TPD. The FTIR result of the used catalysts at 400°C shown in Fig. 7 is more convincing to understand the synthetic effect of KCl and SO_2 because 400°C is close to the SCR reaction temperature of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. Since only NH_4^+ adsorbed on the Brønsted acid sites was observed at 400°C , NH_4^+ may be responsible for the SCR reaction over $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts in the presence of SO_2 , consistent with most of the previous studies [11,13–15,17]. The intensity of the peak at 1427 cm^{-1} follows the decreasing order: K-free-used > K/V(0.3)-used > K/V(0.02)-used > K/V(0.1)-used, which is the same as that of the final X_{NO} shown in Fig. 1(B). This indicates that KCl deposition weakened the catalyst acidity, as reported by several studies [3,4,12,13,15,17,47], and the formation of the eutectics further significantly weakened the acidity. This further indicates that the effect of $\text{V}_2\text{O}_5\text{-K}_2\text{S}_2\text{O}_7$ eutectics on NH_3 adsorption, particularly on NH_4^+ adsorbed on the Brønsted acid sites, may be one of the reasons for the lower X_{NO} of K/V(0.1) and K/V(0.02) catalysts.

In addition to NH_3 adsorption capacity, the other important factor affecting the SCR activity is NH_3 activation, which depends on the oxidation ability of the catalysts. Khodayari et al. [48] and Chen et al. [8] reported that potassium may decrease the redox potential of the surface vanadium species. The oxidation ability of SCR catalysts can be measured by the NH_3 oxidation with O_2 [49–51], where three reactions may occur as indicated by Reactions (3)–(5). In general, the generation of more N_2O and NO indicates the stronger oxidation ability of a catalyst, while the generation of more N_2 indicates the weaker oxidation ability of a catalyst. The requirement of stronger or weaker oxidation ability varies with the type of SCR catalysts [46].



The NH_3 oxidation experiment in this study showed that N_2 was not produced; only NO and N_2O were produced. Fig. 8 shows the NO and N_2O release curves for different used catalysts during NH_3 -TPD. Notably, the rapid increase in NO release observed in K/V(0.02)-used and K/V(0.1)-used catalysts at $\sim 420^\circ\text{C}$ was not because of the NH_3 oxidation with O_2 , but because of the

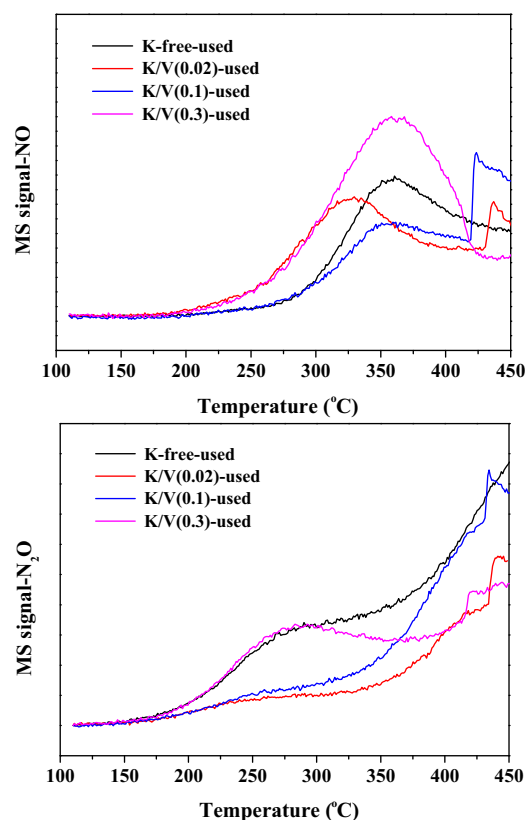


Fig. 8. NO and N_2O releases during NH_3 oxidation on the used catalysts.

reaction of NH_3 with $\text{S}_2\text{O}_7^{2-}$ (as indicated by a large amount of SO_2 release in Fig. 3). Clearly, the NO release by the K/V(0.3)-used catalyst was the most and started at the lowest temperature, while that by the K/V(0.1)-used catalyst was the least and started at the highest temperature. The amounts of N_2O released by the K-free-used and K/V(0.3)-used catalysts were also more than those released by the other two catalysts.

The NH_3 oxidation results indicate that the oxidation abilities of K-free-used and K/V(0.3)-used catalysts were stronger than those of K/V(0.02)-used and K/V(0.1)-used catalysts. This suggests that the formation of $\text{V}_2\text{O}_5\text{-K}_2\text{S}_2\text{O}_7$ eutectics weakened the oxidation ability of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts; however, KCl or K_2SO_4 itself did not decrease the redox potential of vanadium species. The high final X_{NO} values of K-free and K/V(0.3) catalysts indicate that their oxidation abilities are suitable for NH_3 activation or SCR reaction. In contrast, the oxidation abilities of K/V(0.02)-used and K/V(0.1)-used catalysts may be too weak to activate NH_3 , which may be another reason for their low SCR activity.

4. Conclusions

The combined effect of SO_2 and KCl on the SCR of NO with NH_3 using inhouse-prepared $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts was investigated. SO_2 increased the deactivation of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts by KCl, which was only observed after the activity test for 3 h or more. The increased extent depended on the amount of KCl deposited on the catalyst. At a lower K/V molar ratio, 0.02 and 0.1, KCl transformed to $\text{K}_2\text{S}_2\text{O}_7$ and then interacted with V_2O_5 to produce a eutectic. However, at a K/V ratio of 0.3, KCl may have transformed to K_2SO_4 , and the eutectic was not observed. The $\text{V}_2\text{O}_5\text{-K}_2\text{S}_2\text{O}_7$ eutectic significantly decreased NH_3 adsorption, particularly those on Brønsted acid sites, and weakened the oxidation ability of catalysts, thus significantly decreasing the SCR activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.09.036>.

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